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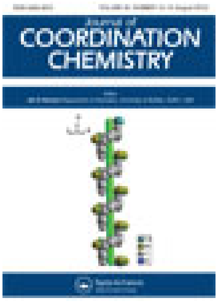

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The role of carboxylic acids in TALSQuEAK separations

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Recent reports have indicated that Trivalent Actinide–Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes (TALSPEAK)-type separations chemistry can be improved through the replacement of bis-2-ethyl(hexyl) phosphoric acid (HDEHP) and diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA) with the weaker reagents 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and *N*-(2-hydroxyethyl) ethylenediamine-*N*,*N*′,*N*′-triacetic acid (HEDTA), respectively. This modified TALSPEAK has been provided with an adjusted acronym of TALSQuEAK (Trivalent Actinide–Lanthanide Separation using Quicker Extractants and Aqueous Komplexes). Among several benefits, TALSQuEAK chemistry provides more rapid phase transfer kinetics, is less reliant on carboxylic acids to mediate lanthanide extraction, and allows a simplified thermodynamic description of the separations process that generally requires only parameters available in the literature to describe metal transfer. This article focuses on the role of carboxylic acids in aqueous ternary (M-HEDTA-carboxylate) complexes, americium/lanthanide separations, and extraction kinetics. Spectrophotometry (UV-Vis) of the Nd^{3+} hypersensitive band indicates the presence of aqueous ternary Nd–Lac–HEDTA species (Lac = lactate, $K_{111} = 1.83 \pm 0.01$ at $1.0\,\mathrm{mol\,L^{-1}}$ ionic strength, $\mathrm{Nd(HEDTA)} + \mathrm{Lac^-} \rightleftarrows \mathrm{Nd(HEDTA)Lac^-}$). While lower levels ($0.1\,\mathrm{mol\,L^{-1}}$ *vs.* $1.0\,\mathrm{mol\,L^{-1}}$) of carboxylic acid will still be necessary to control pH and encourage phase transfer of the heavier lanthanides, application of different carboxylic acids does not have an overwhelming impact on Ln/Am separations or extraction kinetics relative to conventional TALSPEAK separations. TALSQuEAK separations come to equilibrium in two to five minutes depending on the system pH using only $0.1\,\mathrm{mol\,L^{-1}}$ total lactate or citrate.

Keywords: TALSPEAK; TALSQuEAK; HEH[EHP]; HEDTA; Separations

1. Introduction

To enable transmutation of transplutonium actinides, efficient separation of trivalent actinides (An^{3+}) from fission product lanthanides (Ln^{3+}) is needed [1]. Because of the similar hard-acid [2] nature and comparable charge density of An^{3+} and Ln^{3+}, this separation is challenging. The most successful approaches to group separations developed to date have involved exploiting the slightly greater covalency of An^{3+}-bonding interactions, which was first reported by Diamond *et al.* [3]. This difference in bonding characteristics is coincident with the greater radial extension of the 5f orbitals

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(relative to the 4f orbitals in the lanthanides), though it is not yet clear that the effect is indicative of 6d orbital participation in metal–ligand bonding [4–7]. Interaction of nitrogen and sulfur donors with An^{3+} is stronger than with Ln^{3+}, thus potentially enabling a successful separation [5]. This fundamental difference has inspired considerable research addressing the development of soft donor molecules or ions for separations applications [4, 7–12].

One of the most extensively tested approaches to separating trivalent actinides from trivalent lanthanides is the Trivalent Actinide–Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes (TALSPEAK) solvent extraction process and related systems. In TALSPEAK, actinide selectivity over lanthanides arises from the polyaminopolycarboxylate holdback reagent which is balanced against an extractant that does not discriminate between the groups. The origins of TALSPEAK are traced to Oak Ridge National Laboratory in the 1960s [13]. However, complex interactions observed in TALSPEAK chemistry make understanding the fundamental features of the system challenging. Operation of conventional TALSPEAK is characterized by numerous competitive reactions occurring in both the aqueous and organic phases. Arguably, the most problematic organic phase behavior is the partitioning of molar amounts of water and lactate to the organic phase [14, 15]. This serves to consume extractant and could encourage third phase formation. In the aqueous phase, slow phase transfer kinetics hinders equilibrium-based separations in a contactor system and demands high concentrations of carboxylic acid for acceptable system performance [16–19]. These problems appear to arise from application of complexants that are well matched, but probably stronger than necessary for the task at hand.

A recent report has noted the complex interactions observed in TALSPEAK can be sidestepped through the use of a weaker complexant and holdback reagent [15]. Conventional TALSPEAK utilizes bis-2-ethyl(hexyl) phosphoric acid (HDEHP) as the organophosphorus lanthanide extractant and the octadentate aminopolycarboxylate complexant diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA) as the selective americium holdback reagent. The insertion of weaker 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[HEP]) extractant and N-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (HEDTA) in place of HDEHP and DTPA, respectively, significantly reduces the complexity of the system. Structures of these reagents and others relevant to this article can be found in figure 1.

Benefits observed from the HEH[EHP] and HEDTA substitutions include further improvements in predictability of the process performance based on available thermodynamic data, a flat dependence of lanthanide extraction on equilibrium pH, sufficiently improved phase transfer kinetics to contemplate a significant reduction in the concentration of lactate buffer required, dramatically reduced partitioning of both water and lactic acid into the HEH[EHP] extractant phase (relative to HDEHP), and a nearly flat *trans*-lanthanide extraction trend that is approximately consistent with predictions made using thermodynamic data from the existing literature. It is expected that the P–C bond in the phosphonic extractant should exhibit improved resistance to radiolytic and hydrolytic attack of HEH[EHP] relative to HDEHP and would therefore be more robust in application to actual dissolved nuclear fuel solutions. Literature relevant to the radiolysis of HEDTA under TALSPEAK relevant conditions has not been reported thus far, but it is anticipated to behave comparably to the currently utilized DTPA [20–22]. This HEH[EHP] and HEDTA-based TALSPEAK has been

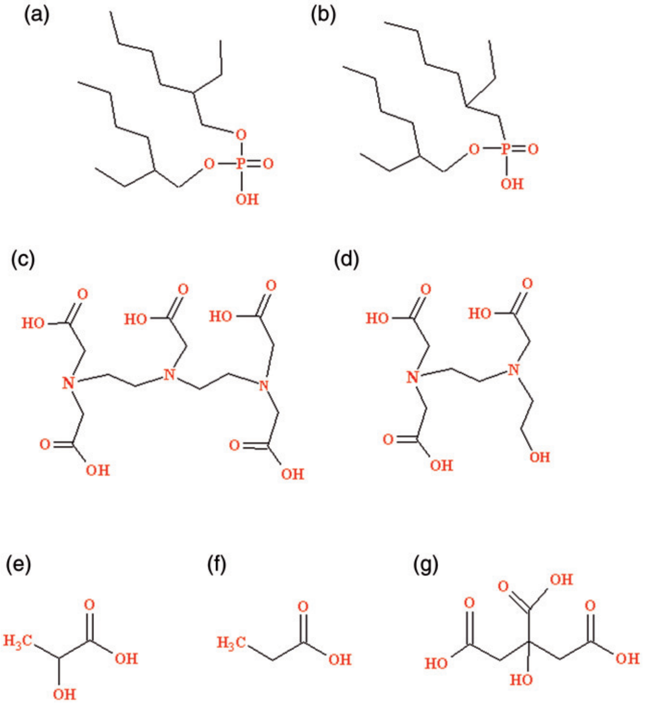

Figure 1. Structures of the components used in these studies; (a) bis-(2-ethylhexyl) phosphoric acid (HDEHP), (b) 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester (HEH[EHP]), (c) diethylenetriamine-N,N,N',N'',N'''-pentaacetic (DTPA), (d) N-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), (e) lactic acid, (f) glycolic acid, (g) citric acid.

provided with the adjusted acronym of TALSQuEAK (Trivalent Actinide–Lanthanide Separation using Quicker Extractants and Aqueous Komplexes).

As with the development of any separation system, increased understanding of the full functioning of various reagents opens the door to more accurate modeling of the system and to possible system optimizations. This report focuses on the role of carboxylic acids in TALSQuEAK. The possibility of aqueous ternary (M-HEDTA-carboxylate) complexes is evaluated, as is the effect of changing the carboxylic acid on lanthanide/americium separation factors and phase transfer kinetics.

2. Experimental

2.1. *Materials*

The HEH[EHP] was procured from Yic Vick Pharmaceutical Company at 90% purity. The third phase formation procedure was used to purify the material to >99% as verified by Nuclear Magnetic Resonance spectroscopy [23]. The *n*-dodecane was obtained from Alfa-Aesar (99% pure) and used as received. Sodium nitrate (Ricca Chemical Company) was dissolved in deionized water, filtered through a 1.0 μm membrane, recrystallized from H_2O and re-dissolved in H_2O to prepare a 5.28 mol $NaNO_3$/kg solution, as determined using Dowex 50 cation-exchange resins (H^+ form) and potentiometric titrations. Sodium chloride for spectrophotometric experiments was filtered using a 20 μm mesh syringe filter. Hydrated lanthanide nitrate salts were obtained from PNNL stocks. The metal content of lanthanide solutions was determined using a Perkin Elmer Optima 7300 DV Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES) in radial mode. For UV-Vis spectrophotometric experiments, an Nd working solution was produced from neodymium oxide by dissolution in reagent-limited perchloric acid providing $Nd(ClO_4)_3$. The Nd concentration in the stock solution was verified by UV-Vis spectrophotometry based on the absorbance of the peak at 576 nm ($\varepsilon = 7.2\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$) [24]. Nitric acid solutions were prepared from Optipure Grade acids (Fisher Scientific) using deionized water obtained from a Milli-Q2 water purification system. Sodium lactate (mixture of D/L isomers) was obtained as an aqueous solution from J.T. Baker and solutions were standardized using cation-exchange chromatography (Dowex 50, H^+ form) with analysis by potentiometric titration. Stock solutions of HEDTA (0.1 mol L^{-1}) were obtained from dissolution of sodium HEDTA salts (Sigma Aldrich). Analytical grade potassium hydrogen phthalate (KHP) was used to standardize the base solutions for potentiometric titrations. Potentiometric titrations were performed using a Ross semi-micro electrode and standardized acid or base. The ^{241}Am and ^{155}Eu tracer in 0.1 mol L^{-1} HNO_3 were obtained from Isotope Products Laboratory, Valencia, CA.

2.2. *Methods*

2.2.1. UV-Vis spectrophotometric titrations. UV-Vis spectrophotometric measurements were made on a 400-series charge-coupled device array spectrophotometer (Spectral Instruments Inc.) with a 200–950 nm scanning range with a 0.35 nm resolution. The solutions were held in quartz 1-cm cuvettes. The temperature was not controlled but the ambient room temperature was established to be 22 ± 1°C. All solution spectra were referenced to a blank solution containing the supporting electrolyte (1.0 mol L^{-1} NaCl). Spectra provided are the baselined average of four thousand scans (four saved files at 1000 scans per file). Chloride was selected as the primary supporting anion to minimize potential spectral interferences that may be associated with high concentrations of nitrate or perchlorate. Spectrophotometric titrations were performed by first introducing a single portion of the starting metal solution directly into the cuvette. The ligand then was introduced by adding aliquots of sodium lactate or HEDTA solution. The change in pH was evaluated by performing a separate experiment in which the pH was measured between lactate or HEDTA additions.

The Fortran-based SQUAD code [25] was employed to refine stability constants and deconvolute molar absorptivities of light absorbing species using non-linear least-square (NLLS) statistics. This code utilizes wavelength and absorbance information initially provided in an ASCII format from the Ocean Optics software. Both multiple regression and NLLS fits were performed and found to be in agreement with each other ($<2\%$ error on the evaluated equilibrium constant). Values provided in this article are based on NLLS routines. Data from 560 to 600 nm and from 725 to 775 nm were used to fit the hypersensitive band and lower energy f–f transition band, respectively. Examination of binary Nd-Lac (Lac = lactate) and Nd-HEDTA system was done to obtain molar absorptivities for individual solution components. Characterized molar absorptivities could then be accounted for in the fitting of a potential ternary species. Alternative species considered in the fitting routine of the ternary experiment included Nd(HEDTA)OH, $Nd(HEDTA)_2$, Nd(H*HEDTA) and the exclusive presence of Nd(HEDTA). The SQUAD program did not minimize to a fit using these models.

2.2.2. Distribution studies. Experiments were conducted at a 1 : 1 (volume) aqueous/organic phase ratio with variations including pH, lactate, and time. Lactate solutions were prepared fresh using sodium lactate rather than lactic acid to minimize possible complications from the lactate esters that form spontaneously in acidic lactic acid solutions. Radiotracer experiments using ^{241}Am and ^{155}Eu were analyzed on an NaI(Tl) solid scintillation counter, a Packard Cobra-II auto gamma, for gross gamma activity. The distribution ratios for extraction using radiotracer techniques were calculated by measuring the amount of radioactivity in both the aqueous and organic phases. The counting efficiency is identical for both phases. The distribution ratio is defined as the ratio of activity of radiotracer in the organic phase to that of the aqueous phase:

$$D_M = \frac{[M]_{f,org}}{[M]_{f,aq}}. \tag{1}$$

The distribution ratios ($[M]_{org}/[M]_{aq}$) for non-radioactive metal ions were calculated by analyzing the aqueous phase before ($[M]_{i,aq}$) and after ($[M]_{f,aq}$) contact with the organic phase. Assuming no losses to sorption or precipitation, and no change in the phase volumes, the difference between $[M]_{i,aq}$ and $[M]_{f,aq}$ defines the concentration of metal in the organic phase. The distribution ratio can then be defined as

$$D_M = \frac{[M]_{i,aq} - [M]_{f,aq}}{[M]_{f,aq}}. \tag{2}$$

Single isotopes were used in the radiotracer experiments, while the ICP-OES experiments were conducted using mixtures of all lanthanides plus yttrium (Pm was excluded due to availability). Acknowledging the potential for wavelength interferences, ICP-OES analysis utilized viewing windows that were not susceptible to such issues. To further confirm the comparability of radiotracer and ICP-OES results, experiments examining ^{155}Eu distribution as a function of metal loading were performed using both radiotracer and inactive metal methodologies with good agreement (within 10%). The total concentration of all metals present in the lanthanide experiments was 14 mmol L^{-1} to prolong extractant availability and allow ICP-OES analysis. Assuming the participation of six HEH[EHP] molecules for metal partitioning, the HEH[EHP] extractant was loaded to 76% of its theoretical capacity. Such high metal loading does impact the system (*vide infra*) and therefore should be acknowledged as a consideration when comparing between separation systems and conditions.

The following conditions were valid for all experimental results reported: (i) experiments were run in duplicate; (ii) all elements were present simultaneously in lanthanide experiments; (iii) concentrations of HDEHP or HEH[EHP] were maintained at

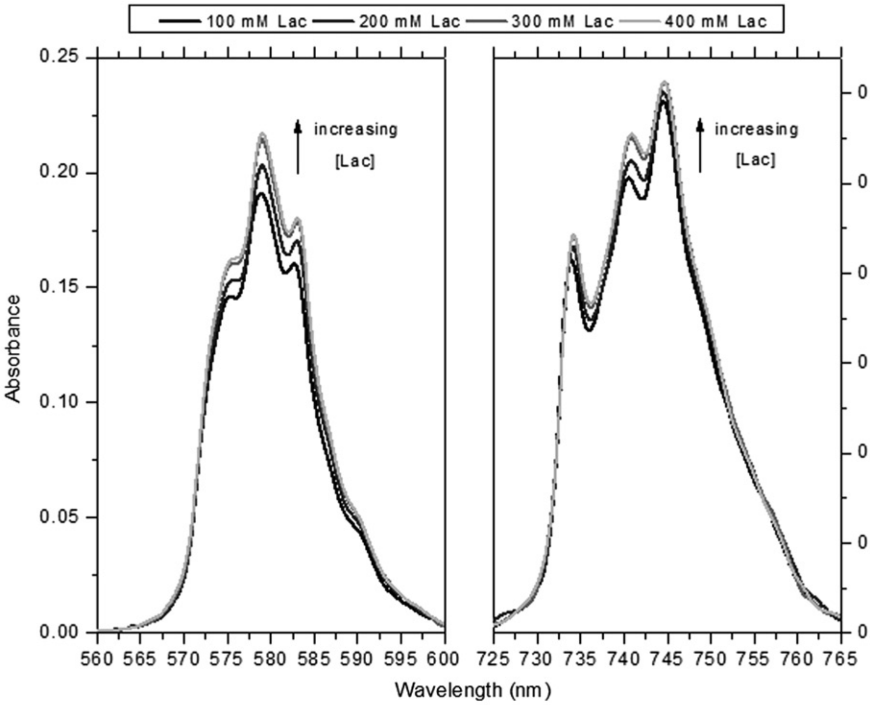

Figure 2. Spectrophotometric titration of lactic acid into an initially 15 mmol L^{-1} $Nd(ClO_4)_3$ and 20 mmol L^{-1} HEDTA solution. The pH and total lactate concentrations are noted in the legend. The Nd^{3+} hypersensitive band and lower energy band from 725 to 760 n mol L^{-1} are shown in the figure. The solution pH at a given concentration of lactate was as follows: 100 mmol L^{-1} – pH 4.63, 200 mmol L^{-1} – pH 4.95, 300 mmol L^{-1} – pH 4.62, 400 mmol L^{-1} – pH 4.78.

0.1 mol L^{-1}; (iv) nitrate (NO_3^-) was present at 1 mol L^{-1}[†]; (v) all experiments were performed at ambient temperature (21 ± 1°C); and (vi) contact times for distribution studies were 30 min, except where otherwise noted and all samples were vortex mixed at 1900 RPM. Previous studies establish that biphasic equilibria for conventional TALSPEAK are attained within these constraints [26].

3. Results

3.1. *Ternary neodymium UV-Vis spectrophotometric investigation*

Spectra of the Nd hypersensitive band from 560 to 590 nm and a lower energy Nd band from 725 to 775 nm are shown in figure 2. While the hypersensitive band is more responsive to changes in metal environment and should generally be used for

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[†] Total ionic strength of the aqueous samples varies with both lactate concentration and pH. In the HEH[EHP] experiments total lactate was 0.1 mol L^{-1} and the ionic strength ranged from about 1.05 to 1.15 mol L^{-1}. The use of NaLac was deemed prudent in experiment design to avoid the complications arising from the lactate esters, lactones, lactides, and polylactates that are known to be present in lactic acid. The salting effect of $NaNO_3$ also improved reproducibility of radiotracer distribution experiments.

Table 1. Equilibrium constants determined in this article and relevant to spectrophotometric fitting and thermodynamic modeling of ternary Nd–Lac–HEDTA species.

Log K_{111} (Nd(HEDTA) + Lac$^-$ $\leftrightarrows$ Nd(HEDTA)Lac$^-$)	
560–600 nm fit	725–755 nm fit
1.87 ± 0.01	1.85 ± 0.01

HEDTA (Literature)

pKa$_1$	pKa$_2$	pKa$_3$	pKa$_4$	pKa$_5$	log $\beta_{101,\mathrm{Nd}}$
(0.5)[a]	(1.6)[a]	(2.33)[a]	(5.48)[a]	(9.73)[a]	14.51 ± 0.01 (14.47)[b]

Lactate (Literature)[a]

pKa$_1$	log $\beta_{101,\mathrm{Nd}}$	log $\beta_{102,\mathrm{Nd}}$	log $\beta_{103,\mathrm{Nd}}$
(3.67)[a]	2.4 ± 0.1 (2.9)[a]	5.3 ± 0.1 (5.6)[a]	6.5 ± 0.1 (6.6)[a]

[a] Ref. [28], 1.0 mol L^{-1} ionic strength.
[b] Ref. [29], 0.5 mol L^{-1} ionic strength.

equilibrium constant determination [27], the lower energy band provided more obvious isosbestic points and therefore allows the more rapid assessment of multiple species in solution. Both peaks were evaluated for the presence of a ternary Nd–Lac–HEDTA species. Using the SQUAD fitting software, logarithmic stepwise equilibrium constants (log K_{111}) of 1.87 ± 0.01 and 1.85 ± 0.01 were established for the ternary species based on the hypersensitive and lower energy band, respectively. These and other relevant equilibrium constants for thermodynamic modeling and spectral fitting are shown in table 1. Acid dissociation constants necessary for spectral fitting were acquired from the NIST Thermodynamic Database and are listed in table 1 [28]. Considering the hypersensitive band is most influenced by changes in the metal environment, the log K_{111} established with the hypersensitive band will be used for all further theoretical modeling.

3.2. *Metal distribution relevant to thermodynamic modeling*

To validate the spectrophotometric result and further the fundamental understanding of the TALSQuEAK system, a pH profile was developed for Nd^{3+} extraction under TALSQuEAK conditions that utilized 1 mmol L^{-1} Nd, 0.1 mol L^{-1} Lac, 20 mmol L^{-1} HEDTA, 1 mol L^{-1} $NaNO_3$, and 0.1 mol L^{-1} HEH[EHP] in *n*-dodecane. Using the stability constant for the ternary Nd–Lac–HEDTA species determined spectrophotometrically, values for HEDTA and lactate metal binding from the NIST database, and HEH[EHP] extraction constants from the literature [30], the predicted partitioning of Nd^{3+} was calculated as described below. Figure 3 shows the calculated Nd^{3+} distribution ratios at 0.1, 0.25, and 0.5 mol L^{-1} lactate, along with the predicted values at 0.1 mol L^{-1} lactate when the ternary species is not taken into consideration. Comparison of the calculated Nd^{3+} distribution ratios to the measured values at 0.1 mol L^{-1} lactate (figure 3) reveals that inclusion of the ternary complex yields a superior thermodynamic description of this extraction system.

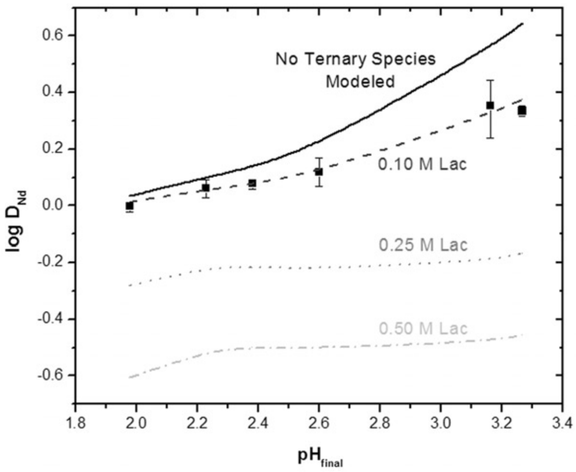

Figure 3. Equilibrium and predicted distribution of neodymium as a function of pH for the TALSQuEAK process. The lines indicate the predicted distribution ratios at 0.1, 0.25, and 0.5 mol L^{-1} total lactate when the ternary Nd–Lac–HEDTA species is accounted for; also shown is the predicted distribution ratios at 0.1 mol L^{-1} lactate when the ternary species is not included in the model (indicated by the "No Ternary Species Modeled" caption). Experimental and modeling conditions include 0.1 mol L^{-1} HEH[EHP], 20 mmol L^{-1} HEDTA. The lactate, neodymium, and nitrate concentration for the experimental set was 0.1 mol L^{-1}, 1.0 mmol L^{-1}, and 1.0 mol L^{-1}, respectively. Contact time was 15 min. Error bars indicate $\pm 3\sigma$ error.

3.3. *Lanthanide-loading studies*

Due to the potential for high lanthanide loading to impact the TALSQuEAK separations system, a set of solvent extraction experiments was developed to compare the partitioning of individual lanthanides at 1 mmol L^{-1} (6% loading) to grouped lanthanides (14 mmol L^{-1} total metal, 76% loading). Figure 4 shows that the distribution of heavier lanthanides (Eu and Gd) is less impacted by the high metal-loading conditions. Lighter lanthanides are more significantly impacted, with La–Nd distribution ratios being approximately an order of magnitude less under high metal-loading conditions. Americium/lanthanide separation also decreases. With 6% metal loading, Am/La separation factors (lanthanum is the least extracted lanthanide in TALSQuEAK) are 40 or more. This is in agreement with previous studies [15]. For the highly loaded system, Am/Ln separations factors are around 15. Therefore, the impact of metal loading should be considered when comparing the following distribution data with other separation systems or studies. High metal loading is not believed to compromise the validity of internal comparisons made between experiments containing different carboxylic acids presented in this report.

3.4. *pH profiles for TALSQuEAK-based systems containing various carboxylic acids*

The pH profiles and separation factor for lactic, citric, and glycolic acids are shown in figure 5. Lactic, citric, and glycolic acids included 0.1 mol L^{-1} carboxylic acid and f-element distribution ratios were studied between pH 2.5 and 3.5. The initial pH range framed for these studies was 2.9–4.5. Therefore, it seems the decreased buffer capacity

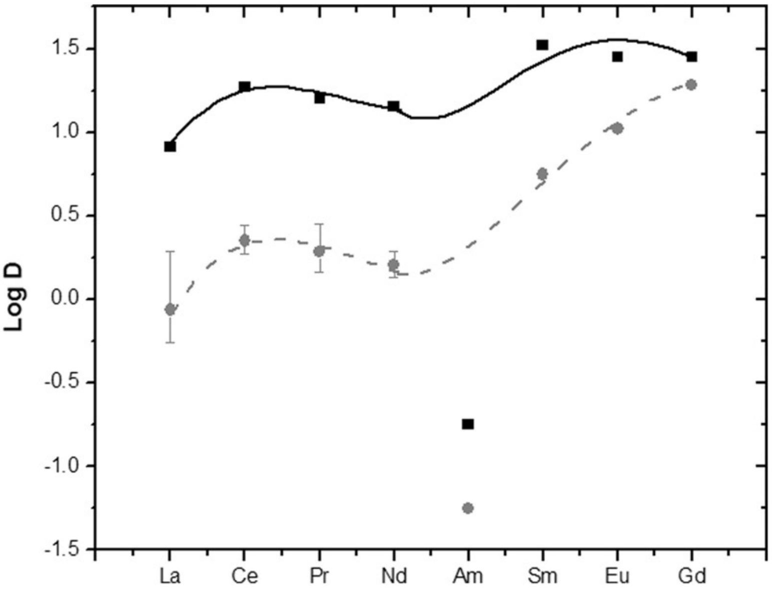

Figure 4. *Trans*-lanthanide distribution patterns for metal-loading variations of the TALSQuEAK process. Squares: low-loading condition; separate measurement for each element with initial aqueous concentration of 1.0 mmol L^{-1}. Circles: high-loading condition; competitive extraction with total initial aqueous lanthanide concentration of 14 mmol L^{-1}. Americium experiments were performed separately, but included non-radioactive lanthanide at the appropriate concentration. The lanthanide used for the low-loading americium distribution study was europium. For all studies, the following were present: *aqueous phase*: 1 mol L^{-1} NO_3^-, pH = 3.6, 0.1 mol L^{-1} total lactate, 20 mmol L^{-1} HEDTA. *Organic phase*: 0.1 mol L^{-1} HDEHP in *n*-dodecane. Contact time was 30 min. Error bars indicate $\pm 3\sigma$ error. The curves drawn are only to guide the eye; they have no mechanistic meaning.

and significant amount of acid released from the HEH[EHP] extractant due to high metal loading lowered the pH. Exchanging the carboxylic acids used in TALSQuEAK has little impact on the Ln/Am separation factor, as most pH profiles start at low pH with very little Am/La separation (average $SF_{pH,2.5} = 2 \pm 2$) and progress to an improved separation at higher pH (average $SF_{pH,3.5} = 16 \pm 2$).

3.5. *Extraction kinetics in TALSQuEAK*

A comparison of lanthanide extraction for equilibrium pH at approximately 2.5 and 4.5 was made for the lactate and citrate-based TALSQuEAK systems. Results are shown in figure 6. Lactate and citrate were selected due to their frequent application in TALSPEAK and TRUSPEAK [31] studies and to their significant structural and electronic differences. Figure 6 shows that the lanthanide extraction kinetics, from a process standpoint, are not significantly impacted by exchanging the carboxylic acid used, at either pH. Metal uptake appears to be impacted by extractant loading. Lighter lanthanides partition to the organic phase first (more rapid kinetics), followed by extraction of the heavier lanthanides. As the heavier lanthanides extract, lighter lanthanides, in part, return to the aqueous phase. Subtle differences appear in lanthanide extraction trends as a function of time. Examination of these differences using relaxation techniques could prove insightful.

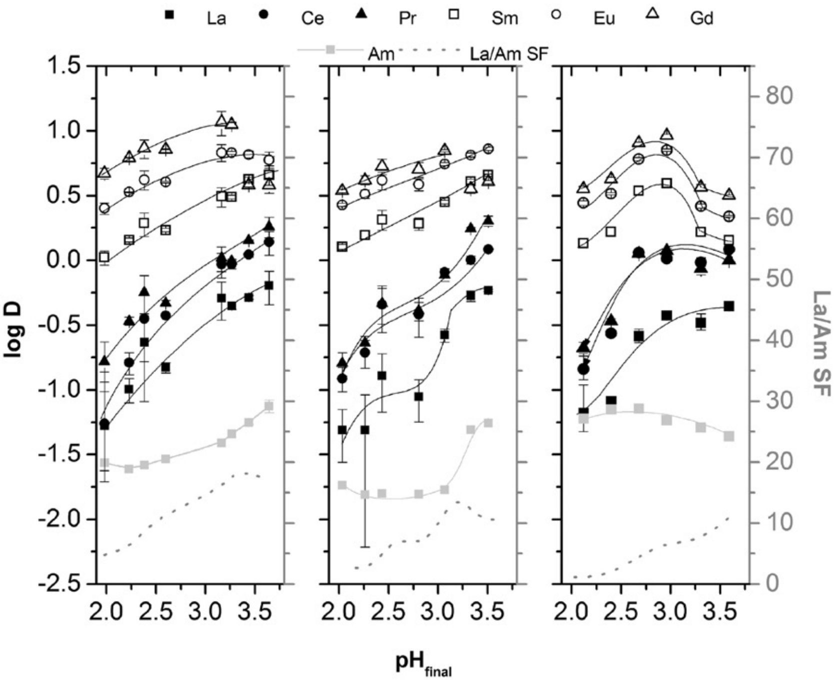

Figure 5. Lanthanide distribution patterns from various carboxylic acid media in TALSQuEAK. Left to right: lactic acid, glycolic acid, citric acid. For all studies, the following were present: *aqueous phase:* 1 mol L^{-1} NO_3^-, 0.1 mol L^{-1} total carboxylic acid, 20 mmol L^{-1} HEDTA, 14 mmol L^{-1} total lanthanide. Nd is excluded to improve graph clarity, but extracted comparably to Pr. *Organic phase*: 0.1 mol L^{-1} HEH[EHP] in *n*-dodecane. Contact time was 30 min. Error bars indicate ± 1σ error. The curves drawn are only to guide the eye; they have no mechanistic meaning.

4. Discussion

4.1. *The role of ternary species in TALSQuEAK separations*

The use of a weaker extractant in TALSQuEAK requires the replacement of the larger DTPA conventionally used in TALSPEAK for the smaller HEDTA americium holdback reagent. While the application of a smaller polyaminopolycarboxylate appears to improve extraction kinetics, some carboxylic acid will still be required to encourage lanthanide transfer to the organic phase. Therefore, the role of ternary species in TALSQuEAK-type separations (those containing smaller sized polyaminopolycarboxylate holdback reagents) will have to be understood for process modeling to be executed. UV-Vis spectrophotometric analysis indicates ternary Nd–Lac–HEDTA species are significant in the TALSQuEAK separations. Evaluation and characterization of the rest of the lanthanide series and the trivalent actinides may become appropriate to allow process monitoring at an engineered scale. Based on observations in HEDTA–iminodiacetic acid–lanthanide studies [32], it seems the stepwise formation constant for ternary lanthanide–HEDTA complexes increases with increasing atomic number (and decreasing ionic radius). This indicates that charge density of the metal center may be more significant in dictating *trans*-lanthanide binding trends than steric factors that would discourage ternary complex formation. Therefore, ternary species,

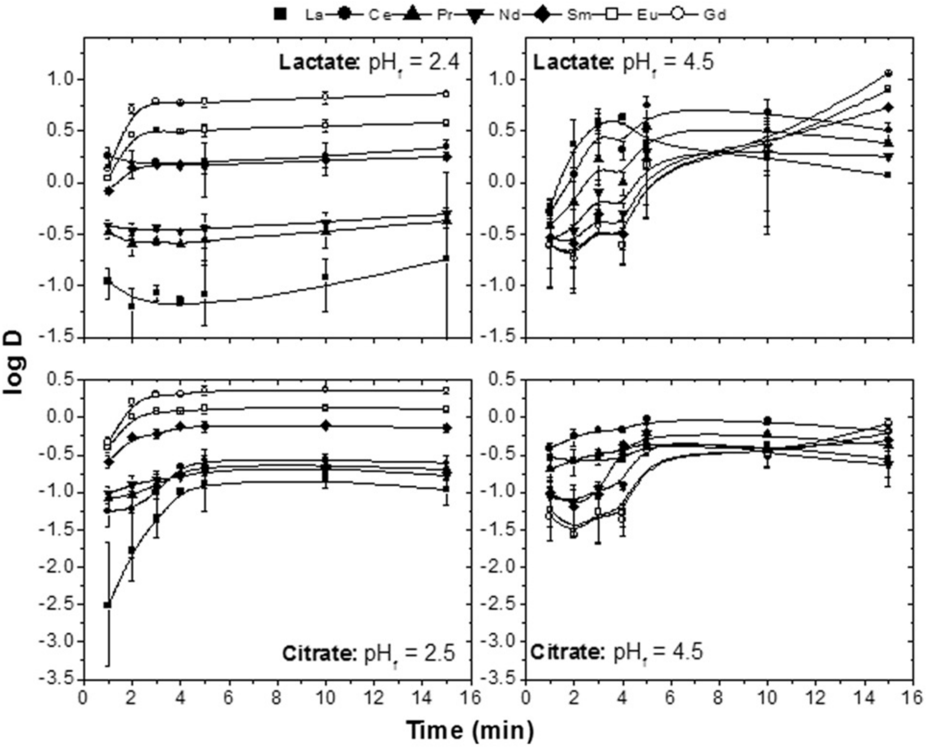

Figure 6. Lanthanide extraction kinetics for variations of TALSQuEAK that include either lactic or citric acid buffer. For all studies, the following were present: *Aqueous phase*: 1 mol L^{-1} NO$_3^-$, 0.1 mol L^{-1} total carboxylic acid, 20 mmol L^{-1} HEDTA, 14 mmol L^{-1} total lanthanide, indicated pH. *Organic phase*: 0.1 mol L^{-1} HEH[EHP] in *n*-dodecane. Error bars indicate ± 1σ error. The drawn curves are only to guide the eye; they have no mechanistic meaning.

and the effects of their presence, should be more pronounced for the heavier lanthanides.

Ternary species in the TALSQuEAK system can both antagonize and improve various dynamic features of the separations process. Figure 3 presents the extraction data and several modeled series for Nd^{3+} extraction as a function of pH and lactate concentration. Using equilibrium constants determined in this work, and others from the literature [16, 28, 30], the effect of ternary species on the TALSQuEAK pH profile was evaluated. The model used is shown here:

$$D = \frac{\overline{[\mathrm{M(AHA)_3}]}}{[\mathrm{M}^{3+}] + [\mathrm{ML}^{2+}] + [\mathrm{ML}_2^+] + [\mathrm{ML}_3] + [\mathrm{MR}] + [\mathrm{MLR}^-]}, \tag{3}$$

where L is lactate, R is HEDTA, and AHA is the singly ionized conventional hydrogen-bonded dimer of HEH[EHP] (H(EH[EHP])$_2$). An in-depth explanation of a similar model used to describe metal distribution in TALSQuEAK systems has been described previously [15, 16, 26].

Calculations show that increasing the lactate concentration reduces the relative increase in Nd^{3+} extraction as the pH increases. A leveled pH profile provided by higher concentrations of lactate would simplify large-scale process control compared to the analogous TALSPEAK system. This flat extraction dependence as a function of increasing pH is provided by increased presence of the ternary species balancing the increased extraction power of HEH[EHP] at higher pH. However, increasing the presence of ternary species could antagonize the separation of the lanthanides from the trivalent actinides. By including another hard-oxygen donor in the selective holdback species that would preferentially contain a large fraction of covalent character, some separation efficiency could be lost. These balancing factors will have to be considered in detail for the development of the most effective TALSQuEAK separations process.

4.2. *Metal loading in TALSQuEAK*

Acidic organophosphorus extractants, such as HDEHP and HEH[EHP], exist primarily as dimers in aliphatic diluents [33]. The dimerization tendencies and cation-exchange properties of these extractants produce the following reaction to describe metal partitioning [33–37]:

$$M^{3+}_{\text{aq}} + \overline{3(HA)_2} \leftrightarrow \overline{M(AHA)_3} + 3H^{+}_{\text{aq}}. \tag{4}$$

Therefore, at low metal concentration for every lanthanide ion extracted, six monomer equivalents of the acidic extractant are required. Used nuclear fuel feeds for a trivalent actinide/lanthanide separations process are projected to contain at least 20 mmol L^{-1} metal ion [38]. A significant amount of acidic extractant (~1 mol L^{-1}) would be required to avoid issues associated with metal loading. However, increasing the extractant concentration in HDEHP and HEH[EHP] extractant systems may encourage organic phase aggregation and alternative extraction mechanisms [15]. In anticipation of these considerations, a cursory examination of metal loading in a TRUSqueak system was performed.

Distribution data presented in figure 4 allows for a couple of observations. The extraction of lighter lanthanides with high metal loading appears to be competitively suppressed by the more favorably extracted heavier lanthanides. Gadolinium, the most charge dense lanthanide in the study, is least affected by additional metal loading. Lanthanum extraction decreases by an order of magnitude in the highly loaded system. Consequently, the separation factor between americium and lanthanum, the least extracted lanthanide, decreases from 40 to 15. These observations indicate application of TALSQuEAK chemistry on more applied feed streams will provide decreased americium/lanthanide separation factors. To ensure these metal loading affects were accounted for in system development, carboxylic acid evaluations were performed at higher metal concentrations.

4.3. *Carboxylic acid variance in TALSQuEAK*

The presence of aqueous ternary complexes in TALSQuEAK increases the probability that buffer substitutions could impact cation partitioning in a different fashion than has been observed in conventional TALSPEAK. TALSQuEAK pH profiles using various carboxylic acids (figure 5) indicates that varying the carboxylic acid has little impact on the separation process. The best americium/lanthanide separations are achieved between pH 3.0 and 3.5 for lactic and glycolic acid. The citric acid profile was expanded to include a higher pH regime (3.5–4.5). At a final pH of 4.0 the separation factor between americium and the least extracted lanthanide (in this case Nd) was 20; however, the preference of engineered operations in TALSPEAK-like separations is to run at a pH closer to 3. In all other cases, lanthanum is consistently the least extracted lanthanide, with little change observed in the rest of the *trans*-lanthanide extraction pattern. The lack of specificity associated with the carboxylic acids could prove advantageous if different carboxylic acids have improved radiolytic stability. Lactic acid minimizes radiolytic degradation of DTPA in conventional TALSPEAK [20]. The capabilities of citrate in this capacity have not been evaluated. However, the lactic acid concentration is known to impact lanthanide extraction kinetics [17–19]. To study the impact of changing the carboxylic acid on system kinetics, a comparative study was performed between lactic and citric acids in the TALSQuEAK system.

The extraction data presented in figure 6 highlight two pH regions. Extraction kinetics in TALSPEAK-like systems are strongly impacted by pH [16]. Though a kinetic mechanism has not been presented for metal extraction in TALSPEAK, lowering the pH expedites lanthanide transfer to the organic phase. The impact of exchanging lactic acid for citric acid in a TALSQuEAK system was examined near pH 2.5 and 4.5. A notable observation is lanthanide extraction is complete for most systems and elements between two and five minutes at 100 mmol L^{-1} carboxylic acid even at higher pH. Previous studies have observed that the phase transfer of heavier lanthanides in conventional TALSPEAK does not reach equilibrium during a 30-minute contact period [19].

Comparison of lactic and citric acid containing systems reveals that system pH is the most significant factor in TALSQuEAK separation kinetics. Probably the most surprising aspect of this study is the inversion of lanthanide extraction trends as a function of pH, regardless of the carboxylic acid used. At lower pH, the extraction of lighter lanthanides (La–Nd) takes longer to reach equilibrium than the heavier lanthanides. At the higher pH, the heavier lanthanides (Sm–Gd) take longer to reach equilibrium partitioning. This result suggests the operation of different rate limiting steps depends on the pH and the size of the cation. It could be argued that the apparently slower kinetics of light lanthanide partitioning arises from the reduced thermodynamic driving force for the phase transfer reaction of the light lanthanides. Conversely, the slow phase transfer kinetics of heavier lanthanides at higher pH may indicate a dominance of the acid catalyzed dissociation process for the lanthanide aminopolycarboxylate species as the dominant feature of the kinetics. Under higher metal-loading conditions, these phenomena may be coupled; it has already been noted that light lanthanides can be displaced from the organic phase by heavy lanthanides.

At pH 4.5, light lanthanide extraction occurs within the first five minutes. After seemingly reaching equilibrium in five minutes, extraction of the heavier lanthanides increases again after 15 minutes of contact. This additional extraction of the heavier lanthanides causes the lighter lanthanides to partially transfer back to the aqueous phase. This is most likely related to the organic phase not being able to solubilize all of the metal present in the system. A slightly faster extraction rate is observed in the lactate system at pH 4.5 compared to the citrate system under similar conditions. The findings of this system indicate more thorough examinations of carboxylic acid effects on the extraction kinetics may be appropriate for TALSPEAK and TALSPEAK-like systems.

5. Conclusion

The roles of carboxylic acids in the aqueous complexation chemistry, actinide/lanthanide separation dynamics, and extraction kinetics have been evaluated for TALSQuEAK separations. Metal extraction in the TALSQuEAK system is quicker and requires less carboxylic acid content than conventional TALSPEAK. Based on Nd^{3+} spectrophotometry, it appears ternary Ln–HEDTA–lactate species are significant in TALSQuEAK chemistry. More investigation quantifying the nature of these ternary species of the rest of the lanthanide series is appropriate. These ternary species provide flat extraction profiles as a function of pH and decrease the fraction of soft donor contribution in the selective holdback reagent complex. The specific carboxylic acid used does not seem to notably impact the trivalent/actinide lanthanide separation, as long as the carboxylic acid can buffer effectively in the pH 3.0–3.5 range. Lanthanide extraction kinetics also appears to be largely unaffected by the carboxylic acid employed, but some nuances, such as changes in the rate of *trans*-lanthanide extraction as a function of pH, may warrant further investigation using more sophisticated kinetic analysis. Ultimately, the lack of process specificity correlated with carboxylic acids in TALSQuEAK could allow flexibility in upstream process development, as increasing process scale may lead to unforeseen complications regarding certain carboxylic acids.

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